

**SURVEY OF ORGANOPHOSPHATE INSECTICIDES  
IN WETLANDS NEAR SUNFLOWER FIELDS  
IN SOUTH DAKOTA**

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Final Report

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Pierre, S.D. 57501-5408

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## Abstract

The Prairie Pothole region of North America contains the most productive waterfowl habitat on the continent. The region also supports intensive agricultural activity that includes routine application of agricultural chemicals to most crops. Insecticides are used mainly on sunflowers, and sunflower acreage in South Dakota has increased more than three-fold since 1990. Parathion is the primary insecticide used on sunflowers and most of it is applied by aerial spraying. Wetlands adjacent to, or encompassed by, sunflower fields are at risk for receiving parathion. Results from the present study suggest that standing water in approximately 25% of the wetlands may contain measurable amounts of parathion. The potential risk to aquatic organisms in wetlands adjacent to sunflower fields is probably underestimated by this study because the detection limit for parathion exceeds the acute limit for the EPA's National Criteria for protection of freshwater organisms. Further study is warranted and should include more sensitive analyses and more attention to factors such as time since last spraying, proximity to sprayed fields, and persistence of parathion in natural wetlands.

Wetlands of the Prairie Pothole region of North America are the most productive waterfowl habitat on the continent (Grue et al. 1986). These wetlands, which formed in depressions left by the retreat of Pleistocene glaciers, also comprise important habitat for resident wildlife and migratory birds other than waterfowl. The Prairie Pothole region also is a major agricultural area where major crops include wheat, oats, barley, hay, and sunflowers (Grue et al. 1986).

Of the agricultural chemicals, insecticides probably pose the greatest threat to wetland wildlife (Grue et al. 1986). They are usually applied by aerial spraying and may enter wetlands via direct (overspray or drift) and indirect (post-application runoff) routes (Grue et al. 1988). Because wetlands are so abundant in the Prairie Pothole region, they are often adjacent to, or encompassed by, cultivated land. Consequently, it is difficult or impossible for pilots to avoid spraying these wetlands (Tome et al. 1991). Moreover, overspray and drift may actually concentrate in wetlands because they occupy depressions in the landscape (Tome et al. 1991). Most of the insecticides now used in the Prairie Pothole region are highly toxic to birds and aquatic invertebrates (Grue et al. 1986, 1988).

South Dakota encompasses about 9% of the North American Prairie Pothole region (Grue et al. 1986). The Prairie Pothole region of South Dakota is an important agricultural area in which there has been a recent expansion in sunflower cultivation (Table 1). Eight counties in this part of South Dakota account for more than 50% of the sunflower acreage in the state. Organophosphate (OP) insecticides, mainly parathion, are commonly used to control the sunflower weevils (*Smicronyx fulvus* and *S. sordidus*) that feed on sunflower seeds. The insecticide is usually applied by aerial spraying in late July or early August (Brad Berven, South Dakota Department of Agriculture, pers. comm.). A

previous study (Tome et al. 1991) in the Prairie Pothole region of North Dakota documented wetland deposition of parathion by aerial spraying, and another documented duck mortality (Grue et al. 1988), but neither study measured parathion concentrations in standing waters.

Recent increases in the acreage planted in sunflowers, and the attendant rise in OP insecticide use, are cause for concern about the fauna in wetlands of the Prairie Pothole region in South Dakota. This study surveys OP insecticides in the standing waters of wetlands that are near sunflower fields.

#### *Methods*

Standing waters in wetlands adjacent to or encompassed by sunflower fields were sampled in eight counties of north-central South Dakota (Figure 1). Thirty-two wetlands were sampled on 18-19 August 1992 and 30 wetlands were sampled on 28 July-2 August 1994.

At each wetland, a water sample was collected in an acid-cleaned glass container with a teflon-lined lid. Samples were stored on ice in the field and refrigerated until they could be shipped to the Fish and Wildlife Service's Patuxent Analytical Control Facility (PACF) for analysis. Samples from 1992 were extracted on 21 September and analyzed on 23 September; samples from 1994 were extracted on 24 August and analyzed on 26 August. QA/QC procedures at the PACF followed the Service's protocol and all duplicates and spikes were within acceptable limits. In 1994, nine samples were split and the duplicate also was sent to the Hygienic Laboratory at the University of Iowa where samples were extracted on 5 August and analyzed 8-9 August. Both laboratories assayed samples for a scan of 24 OP insecticides (Table 2). The

detection limit for analyses from the PACF was 2 µg/l and the quantitation limit for analyses at the Hygienic Lab was 0.1 µg/l.

### *Results*

Of the 62 wetlands surveyed, eight contained detectable amounts of four OP insecticides (Table 3). Parathion was the most commonly encountered OP insecticide; it was found in seven wetland ponds. Three of those seven ponds also contained measurable amounts of methyl parathion. The remaining pond had small amounts of fenthion and monocrotophos.

Samples split with the Hygienic Laboratory showed reasonable consistency with those analyzed by the PACF. In two instances the Hygienic Laboratory detected parathion and methyl parathion at levels below the detection limit for the PACF. In six of the samples neither lab detected OP pesticides. In one sample, both labs found measurable amounts of parathion and methyl parathion, although results from the PACF were a factor of 3 lower than those obtained by the Hygienic Lab. The lower concentrations reported by the PACF may reflect the effect of longer time elapsed between sample collection and extraction at PACF than at the Hygienic Lab (cf. APHA 1992).

### *Discussion*

OP insecticides were encountered in relatively few of the wetlands surveyed in the sunflower growing region of South Dakota. In addition, parathion (including methyl parathion) was the predominant OP insecticide. Parathion is the primary insecticide sprayed on sunflowers (Bruce Jacobson, South Dakota Department of Agriculture, pers. comm.). The detection of fenthion and monocrotophos in one wetland in 1992 is

puzzling because neither insecticide is associated with sunflower production.

The relatively low frequency of parathion detection in Prairie Pothole wetlands is surprising because these wetlands are close to cultivated sunflower fields. It is, however, consistent with a previous survey of 6 OP insecticides (not including parathion) in wetlands associated with corn fields in eastern South Dakota (Ruelle and Henry 1993). The low frequency of parathion occurrence implies either that insecticides had not been sprayed in the area, or the time elapsed since the most recent spraying was sufficient to allow for the degradation of the pesticide.

Parathion is used chiefly to control sunflower weevils. The abundance of weevils varies in space and time, and it is not always necessary to apply the insecticide to the fields. For example, the acreage sprayed varied from 2 - 85% depending on the county and year (Table 4). If wetlands were chosen at random in a county, the frequency of parathion detection should be similar to the proportion of fields that were sprayed. However, parathion was not detected in any of the wetlands in 1992 even though 40% of the fields had been sprayed.

The second factor affecting the frequency of parathion occurrence at a point in time is the degradation of the pesticide under natural conditions. If hydrolysis were the only process by which parathion were degraded in the environment, its half life would be on the scale of 100 to 300 days depending on pH (Racke 1992). In natural aquatic systems, however, the affinity of OP insecticides for sediment particles tends to remove the insecticides from the water column very quickly; the half life in a pond may be less than two days (Racke 1992). If so, an

initial concentration of 10  $\mu\text{g/l}$  would be undetectable (less than 2  $\mu\text{g/l}$ ) in less than a week.

Despite the relatively low concentrations of parathion detected in some wetlands, the concentrations detected could cause acute toxicity problems for many aquatic organisms (Table 5). In particular, herbivorous cladocerans at the base of the aquatic food web (e.g., *Daphnia*) are extremely sensitive to parathion at concentrations less than 1  $\mu\text{g/l}$  (Brown 1978). National criteria for exposure of freshwater organisms have been set at 0.065  $\mu\text{g/l}$  and 0.013  $\mu\text{g/l}$  for acute and chronic levels, respectively (USEPA 1986). These criteria are below the detection limits available for this study.

In general, the immediate and short-term effects on pond organisms are predictable from lab toxicity studies, but the long-term effects are not so easily predicted. For example, *Daphnia* eliminated by the acute toxicity of parathion did not return to the water column for about 10 weeks after initial exposure (Muirhead-Thomson 1987).

Water column concentrations of OP may not present the complete picture for some organisms. Although OP insecticides are not generally considered susceptible to bioconcentration (Manahan 1994), there are reports of bioconcentration occurring in some aquatic organisms. For example, *Gambusia* accumulated parathion to a level 335x ambient (Brown 1978) and tadpoles showed concentrations 64x ambient (Hall and Kolbe 1980). Therefore, tadpoles and fish in these pothole wetlands may be more at risk than would be evident from their relatively high tolerance to acute exposure.

The detection limit for measuring parathion in most of the analyses performed for this study was higher than concentrations known to be



toxic to aquatic organisms. Consequently, it is not known how many of the 55 wetlands with no detectable parathion actually contained levels toxic to *Daphnia*, for example. It is possible to speculate, however, by using information from the samples split with the Hygienic Lab, which performed a more sensitive assay (0.1 µg/l). Of the 8 samples with parathion less than 2 µg/l (according to the PACF), 2 (25%) had concentrations greater than 0.1 µg/l. By extrapolation, an additional 13 wetlands may have had parathion at concentrations between 0.1 and 2 µg/l.

It has been hypothesized that at least part of the decline in waterfowl populations from 1972-1985 was the result of increased use of insecticides (Grue et al. 1988). No definitive answer is available at this time, but recent data (Anonymous 1994) suggest that habitat availability is a strong component of waterfowl success. Recent wet years have increased the number of wetlands available during the breeding season and there has been a strong recovery of waterfowl populations. It is clear that insecticides can cause loss of waterfowl, but the scale of loss is not known, and there are not enough data to speculate on potential losses due to insecticides.

Despite the relatively low frequency of parathion detection in wetlands associated with sunflower fields, the fauna of those wetlands may be at risk. In addition, it is difficult or impossible for pilots to avoid spraying wetlands that are within or adjacent to the boundaries of fields, the potential risk is high. A more comprehensive study is needed to assess the actual risk to aquatic organisms and other wildlife associated with prairie pothole wetlands because the analytical techniques available for this study were not sufficiently sensitive and

because there was inadequate information on the time elapsed since the most recent spraying.

#### *Recommendations*

- 1) Determine the number of wetlands or density of wetlands associated with sunflower fields in the prairie pothole region of South Dakota. Primary focus should be placed on those wetlands managed by the Service. If the number is small it may not be worth pursuing the issue further. If the number is large, however, the following item should be considered.
- 2) Repeat the study but with more attention to critical factors that may determine the exposure and risk of the organisms.
  - a. Time since most recent spraying. Greater cooperation will be required with individual land owners and possibly with the South Dakota Department of Agriculture.
  - b. Include a time series of samples from one or more wetlands. These should be on a daily basis for as much as a week after the insecticide has been applied.
  - c. Measure parathion with instrumentation that will register concentrations as low as the National Criteria (0.01 µg/l).

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Table 1. Acres of sunflowers planted in South Dakota counties where wetland waters were collected for OP insecticide evaluation.

| County             | 1988    | 1989    | 1990    | 1991    | 1992    | 1993    | 1994    |
|--------------------|---------|---------|---------|---------|---------|---------|---------|
| Beadle             | 11,400  | 16,400  | 24,000  | 38,800  | 36,900  | 58,900  | 74,700  |
| Brown              | 16,700  | 14,900  | 20,400  | 37,200  | 30,900  | 54,500  | 93,000  |
| Faulk              | 16,700  | 20,000  | 14,800  | 19,400  | 19,300  | 29,300  | 42,100  |
| Hand               | 21,300  | 26,400  | 26,300  | 33,400  | 34,800  | 49,100  | 64,000  |
| Hughes             | 6,100   | 4,200   | 6,600   | 14,000  | 13,000  | 17,800  | 19,700  |
| Potter             | 11,400  | 10,300  | 8,100   | 11,500  | 11,700  | 21,400  | 28,300  |
| Spink              | 17,700  | 23,900  | 27,600  | 40,600  | 38,900  | 64,200  | 96,300  |
| Sully              | 30,000  | 34,900  | 29,200  | 47,900  | 43,100  | 57,200  | 74,700  |
| Subtotal           | 131,300 | 151,000 | 157,000 | 242,800 | 228,600 | 352,400 | 492,800 |
| Statewide<br>Total | 260,000 | 300,000 | 300,000 | 450,000 | 400,000 | 650,000 | 940,000 |

Table 2. List of organophosphate insecticides that could be detected in the analytical scan performed by the Patuxent Analytical Control Facility. The detection limit was 2 µg/L.

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|                 |                  |
|-----------------|------------------|
| Acephate        | Famphur          |
| Azinphos-Methyl | Fenthion         |
| Chlorpyrifos    | Fensulfothion    |
| Coumaphos       | Malathion        |
| Demeton         | Methamidophos    |
| Diazinon        | Methyl Parathion |
| Dichlorvos      | Mevinphos        |
| Dicrotophos     | Monocrotophos    |
| Dimethoate      | Parathion        |
| Disulfoton      | Phorate          |
| Ethoprop        | Terbufos         |
| EPN             | Trichlorfon      |

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Table 3. Concentrations ( $\mu\text{g/l}$ ) of organophosphate insecticides measured in waters of South Dakota wetlands associated with sunflower fields. All samples were analyzed at the Patuxent Analytical Control Facility (detection limit =  $2 \mu\text{g/l}$ ). Splits from nine samples (SF-94-22 through SF-94-30) were also analyzed by the Hygienic Laboratory at the University of Iowa (quantitation limit  $0.1 \mu\text{g/l}$ ).

|                     | Wetland  | County | Concentration |      |
|---------------------|----------|--------|---------------|------|
|                     |          |        | PACF          | Iowa |
| Parathion           | SF-94-1  | Sully  | 68            | NA   |
|                     | SF-94-8  | Sully  | 3             | NA   |
|                     | SF-94-9  | Sully  | 2             | NA   |
|                     | SF-94-10 | Hand   | 5             | NA   |
|                     | SF-94-22 | Brown  | ND            | 0.5  |
|                     | SF-94-24 | Brown  | 29            | 100  |
|                     | SF-94-25 | Spink  | ND            | 0.9  |
| Methyl<br>Parathion | SF-94-22 | Spink  | ND            | 0.2  |
|                     | SF-94-24 | Brown  | 13            | 37   |
|                     | SF-94-25 | Spink  | ND            | 0.2  |
| Fenthion            | SF-92-17 | Beadle | 6             | NA   |
| Monocrotophos       | SF-92-17 | Beadle | 6             | NA   |

NA = not analyzed

ND = not detected

Table 4. Acreage of sunflower fields sprayed aerially with parathion or methyl parathion. Data from Commercial Applicator Spray Report Summary provided by Bruce Jacobson, South Dakota Department of Agriculture.

| County | 1992             |                       | 1993             |                       |
|--------|------------------|-----------------------|------------------|-----------------------|
|        | acres<br>sprayed | % of acres<br>planted | acres<br>sprayed | % of acres<br>planted |
| Beadle | 6,904            | 61                    | 31,391           | 85                    |
| Brown  | 5,050            | 30                    | 10,025           | 32                    |
| Faulk  | 10,448           | 63                    | 7,941            | 41                    |
| Hand   | 17,637           | 83                    | 15,814           | 45                    |
| Hughes | 3,919            | 64                    | 2,131            | 16                    |
| Potter | 8,248            | 72                    | 251              | 2                     |
| Spink  | 4,082            | 23                    | 5,854            | 15                    |
| Sully  | 15,202           | 51                    | 12,542           | 29                    |
| Total  | 71,490           | 54                    | 85,949           | 38                    |

Table 5. Median lethal concentration (LC<sub>50</sub>; µg/l) for 48h exposure to parathion for selected aquatic organisms. Data from Brown (1978), USEPA (1975 and 1986).

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|                                      |        |
|--------------------------------------|--------|
| Insecta                              |        |
| <i>Pteronarcella badia</i>           | 5.6    |
| <i>Claasenia sabulosa</i>            | 3.5    |
| <i>Chironomus tentans</i>            | 31     |
| Crustacea                            |        |
| <i>Daphnia magna</i>                 | 0.8    |
| <i>D. carinata</i>                   | 0.5    |
| <i>D. pulex</i>                      | 0.6    |
| <i>Simocephalus serrulatus</i>       | 0.4    |
| <i>Gammarus fasciatus</i>            | 0.4*   |
| <i>Palaemonetes kadiakensis</i>      | 12*    |
| Amphibia                             |        |
| <i>Pseudacris triseriata</i> tadpole | 1000** |

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\*24 h  
 \*\*96 h



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